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1,4-DEHYDROBENZENES

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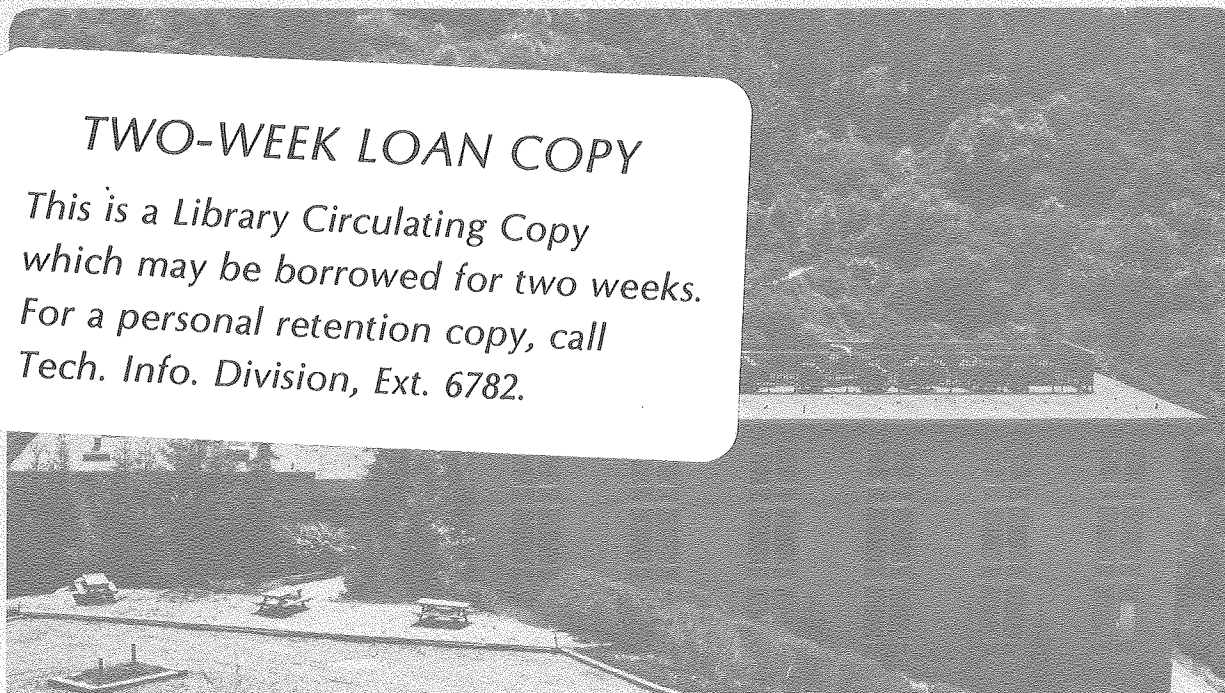
DETERMINATION OF THE REACTIVE SPIN STATE OF 1,4-DEHYDROBENZENES

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Abstract

Two approaches have been used to determine the spin state(s) of 1,4-dehydrobenzenes produced in the solution reaction of diethynyl olefins. The first method relies on the "spin correlation effect" which postulates a relationship between the spin state of a caged radical pair and the ratio of cage and escape reactions (C/E) which may occur in the pair. When the 2,3-di-n-propyl-1,4-dehydrobenzene biradical (4) abstracts hydrogen from 1,4-cyclohexadiene, a radical pair is generated. If a mixture of 1,4-cyclohexadiene-d_0 and -d_4 is employed it is possible, by performing a VPC-MS analysis, to determine the ratio C/E leading from the radical pair to the reduced product, o-dipropylbenzene 10. Applying this method to the reaction of Z-4,5-diethynyl-4-octene (3), C/E was found to be 0.6, independent of the concentration of 1,4-cyclohexadiene (between 0.1 and 10 M) in the chlorobenzene reaction solution. This result suggests the presence of the singlet state of 4 in the reaction of 3. Independent support for this analysis came from the reaction of 3,4-dimethyl-1,5-diyn-3-ene (11) in hexachloroacetone solvent in an NMR probe. The major product, 1,4-dichloro-2,3-dimethylbenzene (12), obtained by chlorine abstraction from the solvent, showed CIDNP polarization (emission) in the aromatic protons. The interpretation

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of this result is straightforward and indicates solvent trapping of the singlet state of the intermediate 2,3-dimethyl-1,4-dehydrobenzene. Both of these experiments indicate that only the singlet state of 1,4-dehydrobenzenes is generated upon thermal reaction of diethynyl olefins. The failure to observe evidence for the triplet state of the 1,4-dehydrobenzenes under the reaction conditions requires that, if the triplet is the ground electronic state, the rate of intersystem crossing from the singlet must be $<10^9 \text{ sec}^{-1}$.

Introduction

In spite of the efforts of numerous investigators to generate and study the chemistry of 1,4-dehydrobenzene (1),[1,2] the spin states populated under the reaction conditions have yet to be characterized. This is a particularly intriguing problem because the singlet and triplet states are presumed to be close in energy and because of the failure of theoretical treatments to reach a consensus in predicting the ground electronic state (Table 1).[3-8]

Wilhite and Whitten[4] reported a detailed ab initio study in which three calculations were performed: a full SCF-MO treatment of both the singlet and triplet electronic states, a limited configuration interaction (CI) calculation, and a many-determinant CI treatment. The simplest calculation predicted that the energy of the triplet biradical lies well below that of the singlet. Inclusion of CI in the calculations, however, led to a much smaller predicted difference in the singlet and triplet biradical energies. The smallest energy difference was predicted in the full CI calculation which placed the triplet state 3.5 kcal/mole below the singlet. In these calculations, the geometry of 1,4-dehydrobenzene was somewhat arbitrarily taken to be that of benzene. Wilhite and Whitten were careful to point out that, given the small singlet-triplet energy difference found, a calculation performed at the equilibrium geometry might lead to an inverted ordering of the electronic states. Because the geometry was fixed in their treatment, no prediction was made concerning the relative positions on the energy surface of the diradical structure 1a and its bicyclic isomer butalene 1b(which would be expected to have a much shorter 1,4 distance than benzene).

Dewar and Li[5] reported a MINDO/3 study in which geometry optimization was carried out for the singlet and triplet electronic states. The singlet

1a   1b   2
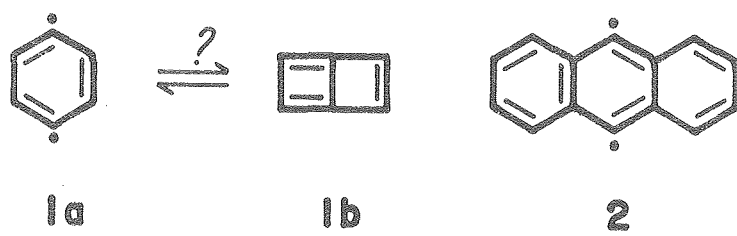
biradical was predicted to be 6.2 kcal/mole more stable than the triplet. An investigation of the singlet surface led to the prediction that butalene lies in a relative energy minimum, 35.9 kcal/mole above the singlet biradical. The transannular bond in butalene was predicted to be 1.667 A long.

A generalized valence bond (GVB) calculation of the 1,4-dehydrobenzene energy surface was recently reported by Noell and Newton.[6] These authors performed limited geometry optimization for the singlet and triplet states. They concluded that the lowest energy structure of 1,4-dehydrobenzene is the singlet biradical and that the bicyclic butalene structure lies in a local energy minimum very roughly estimated to be 77 kcal/mole higher. The triplet biradical was calculated to have an energy slightly above that of the singlet (1.4 kcal/mole), though the difference calculated for the two biradicals appears to be less than the uncertainty of the calculations.

To date, the only reported experimental attempt to determine the spin state of a 1,4-dehydroaromatic is that of Chapman and coworkers[9], who generated 9,10-dehydroanthracene (2) in a matrix at 8° K and searched, without success, for an ESR signal which would have indicated population of the triplet state. In this paper we detail our efforts to determine the number and description of the reactive spin states of the 1,4-dehydrobenzenes generated by the thermal reaction of diethynyl olefins at higher temperatures in solution. Our approach includes both chemically induced dynamic nuclear polarization (CIDNP) and chemical trapping experiments.

Results and Discussion

As previously reported,[2] when 3 (Scheme I) was heated in a ^{1}H-NMR probe at 160° C, emission was observed in the signals due to vinyl and terminal methyl and methylene protons. The location of the

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protons in 9 which showed emission indicates that biradical 7 is the molecule in which the CIDNP effects arose. The following observations are inconsistent with $S-T_0$ mixing and indicate instead an $S-T_-$ mixing mechanism:[10] (1) The protons α and β to the radical centers showed the same polarization; this indicates that the sign of the hyperfine interaction has no effect on the spectrum. (2) All of the polarized signals were emissive; normally, for polarizing radicals with a g-value difference of zero, a mixture of enhanced absorption and emission (multiplet effect) is observed. The $S-T_-$ mechanism has been observed at high magnetic fields only in small biradicals (unpaired electrons separated by fewer than ca. 10 carbon atoms).[10,11]

Closs[10] has delineated two mechanisms by which the CIDNP effects observed in 9 may be explained: if singlet 7 is present and is higher in energy than triplet 7, emissive signals may be observed if there exists a bimolecular reaction channel which drains off the triplet biradical formed by magnetic field-induced intersystem crossing (isc, Scheme II). On the other hand, if triplet 7 is produced in the reaction (by magnetic field independent intersystem crossing in either 4, 6 or 7) and the ground state of biradical 7 is a triplet, then T_--S mixing can produce the observed signals, even in the absence of a spin-selective reaction channel. This analysis indicates that either singlet or triplet 7 may produce the observed polarizations; furthermore, it is difficult to distinguish between these possibilities on the basis of the experimental observations. If the triplet of 7 is produced in the reaction of 3, three distinct modes of population of the triplet manifold are possible. Intersystem crossing in the 1,4-dehydrobenzene biradical, 6 or 7 could all have led to the formation of some fraction of 7 in the triplet state. Thus, even if triplet 7 is present it cannot be

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determined unambiguously in which of the three biradicals intersystem system crossing occurred.

A more straightforward CIDNP analysis may be obtained by looking for polarization effects in the products of bimolecular reaction of the 1,4-dehydrobenzene biradical. This approach has been successfully applied in the thermal reaction of 2,3-dimethyl-hexa-1,5-diyn-3-ene (11; Scheme III). When a solution of 11 in hexachloroacetone (0.1 M) was heated to 160° C in the probe of a 90 MHz ^{1}H-NMR spectrometer, the spectrum obtained showed an emission in the aromatic region (Fig. 1). VPC analysis of the solution after reaction showed the formation of 1,4-dichloro-2,3-dimethylbenzene (12) and 1-chloro-2,3-dimethylbenzene (13) (relative yields, ca. 3:1). Only minor amounts of other products were detected by VPC. The emission observed during the thermal reaction of 11 is assigned to the aromatic protons of 12. The broad proton absorption in the alkyl region (Fig. 1, spectrum (C)) is attributed to polymerization products formed as a result of the relatively high concentration of 11 in the NMR experiment.

Thermal reaction of dilute solutions of 11 (0.01 M) in hexachloroacetone and CCl_4 gave results (Table 2) similar to the NMR experiment. Product 12 was isolated from a CCl_4 solution reaction by preparative VPC and characterized by IR, ^{1}H-NMR and HRMS.

The mechanism shown in Scheme III is proposed to explain the reaction of 11 in hexachloroacetone. By analogy to the thermal chemistry of 3, cyclization of 11 gives the 2,3-dimethyl-1,4-dehydrobenzene biradical (14) which may abstract chlorine from solvent to produce a solvent-caged radical pair. Cage escape of the aryl radical (15) and abstraction of a second chlorine atom from the solvent gives 12. Hydrogen abstraction reactions of 14 and 15 lead to 13. The pentachloroacetonyl radicals generated by loss of

chlorine may attack 11; this is presumed to be responsible for the modest yield of aromatic products.

The observed polarizations can be readily interpreted by application of Kaptein's rules[12] (equation 1). Because the aromatic signal appeared in

$$\Gamma = \mu\epsilon\Delta g A_i \qquad (1)$$

emission, the product of the four parameters must be ($-$). Compound 12 was formed by escape from the polarizing pair; therefore ϵ is negative ($-$). The g value of 15 should be less than that of the pentachloroacetonyl radical (cf. g values of phenyl (2.0025) and dichloromethyl (2.0080))[13] so $\Delta g = (-)$. The hyperfine coupling constant in phenyl radicals is positive for the ortho, meta and para hydrogens, so $A_i = (+)$. The remaining parameter, μ, must be assigned a value which makes the product of the right hand side negative since the polarization in 12 was emissive; the sign of μ, therefore, is ($-$) which indicates that the spin state of the polarizing radical pair is singlet. The singlet spin state of 1,4-dehydrobenzene 14 therefore must be the predominant source of product.

The CIDNP observed in 9 may be reinterpreted in light of the findings for 14 by postulating that the polarizations either arose from singlet 7 or that triplet 7 was produced as a result of intersystem crossing in biradical 6 or 7 but not in the 1,4-dehydrobenzene biradical.

Chemical Trapping Studies

A second approach to determining the spin states present in solution involves an attempt to distinguish between the chemical reactivity of the triplet and singlet states of 1,4-dehydrobenzene 4. Because radical pairs are generated by abstraction reactions of 4, the task reduces to finding a way to differentiate the reactivity of singlet and triplet radical pairs.[14]

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The spin correlation effect (SCE)[15] postulates that radical pair reactivity is related to the spin state of the pair: singlet radical pairs may undergo both cage[16] and escape reactions but a spin prohibition against cage reactions limits triplet radical pairs to cage escape (in the absence of intersystem crossing).[17] In order to detect the presence of singlet and triplet radical pairs generated by trapping of singlet and triplet 4, we must distinguish between the cage and escape pathways leading to product formation; the magnitude of the ratio of cage/escape reactions should reflect the spin state of the radical pair generated from 4.

Scheme IV illustrates the cage and escape reactions that can occur in the radical pair generated by hydrogen transfer from 1,4-cyclohexadiene to biradical 4. While the combination products (see ref. 2b for possible structures of these materials) are unique to cage reaction,[18] 10 is produced both by cage disproportionation and cage escape; it is necessary, therefore, to determine the extent to which the cage and escape reaction pathways contribute to the yield of 10. It is possible to perform this analysis if a mixture of 1,4-cyclohexadiene-d_0 and -d_4 is used in the reaction solution. Consider first the reaction of 4 with cyclohexadiene-d_0. The cage reactions which the radical pair (formed by hydrogen transfer to 4) may undergo include transfer of a second hydrogen atom to give 10-d_0 and combination to produce C_{18} products. Escape of the aryl radical from the solvent cage, followed by abstraction of hydrogen or deuterium from trapping agent will give 10-d_0 and -d_1 in the ratio 1:1 in the absence of a deuterium isotope effect. By a similar analysis, if 4 initially interacts with deuterated trapping agent, 10 formed by cage reaction will contain two deuteria while cage escape will lead to 10-d_1 and -d_2 in the ratio 1:1. In summary, cage reaction will lead to only 10-d_0 and -d_2 (1:1 ratio) and escape reactions of the radical pair

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should give $10\text{-}d_o$, $-d_1$ and $-d_2$ in the ratio 1:2:1. Because $10\text{-}d_1$ is unique to the cage escape reaction channel, it is possible to dissect the experimentally observed ratio of $10\text{-}d_o$, $-d_1$ and $-d_2$ (obtained by mass spectroscopic analysis) into the relative contributions of the cage and escape pathways; when the yield of combination products is added to the yield of 10 produced by cage reaction, the ratio of cage to escape products (C/E) is obtained.

It is impossible to predict, a priori, the relative amounts of cage and escape reaction for a given singlet radical pair (the SCE postulates that C/E for a triplet pair is zero). For this reason an experimentally observed ratio of C/E by itself will provide limited quantitative information about the relative amounts of singlet and triplet 4 present in solution. The analysis is broadened, however, by consideration of the kinetic relationships in Scheme V. Conservation of spin (in the cyclization reaction) requires that biradical 4 is initially generated in the singlet state. The ratio of trapping of the singlet biradical to intersystem crossing to triplet 4 will depend on the concentration of trapping agent in solution.[19] At low concentrations of cyclohexadiene intersystem crossing should be at its maximum value whereas a high concentration of the trapping agent will increase $k_T[SH]$ and the amount of intersystem crossing observed should be at a minimum.

Compound 3 (0.01 M) was allowed to react at 195° C in a chlorobenzene solution which contained added cyclohexadiene (d_o:d_4 = 1:4) ranging in concentration from 0.01 M to 10.6 M. The data obtained by combined VPC and VPC-MS analysis are plotted in figure 2. The ratio C/E (0.55) did not vary, within experimental error, over the range 0.2 to 1.6 M cyclohexadiene. The ratio of C/E was experimentally difficult to determine for the entire product

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spectrum at low concentrations of cyclohexadiene;[20] the ratio of C/E for

product 10, however, may be readily determined by VPC-MS analysis alone. As

the lower plot in figure 2 shows, the ratio of C/E for product 10 (0.20) was

independent of cyclohexadiene concentration from 0.01 to 10.6 M. The

relatively large, constant value of C/E for the complete product spectrum

(ca. 0.55) indicates the presence of the singlet radical pair generated from

the singlet state of 4.

If the ground state of 4 is a triplet but intersystem crossing from the

singlet is slow relative to unimolecular and bimolecular reaction, exclusive

trapping of the singlet state will be observed at all concentrations of

cyclohexadiene. One way to increase k_{isc} is to perform the reaction in a

brominated solvent; the presence of bromine either in a reacting substrate or

in the solvent is known from excited state chemistry to increase intersystem

crossing rates (the heavy-atom effect).[21] When 3 was allowed to react in

bromobenzene solution, the ratio of C/E was found again to be independent of

cyclohexadiene concentration (figure 3). As before, the large value of C/E

(ca. 0.64) suggests the exclusive formation of the singlet radical pair. The

ratio C/E for product 10 (0.20) was also independent, within experimental

error, of the concentration of cyclohexadiene.

In a previous study it was shown that both 4 and 6 are trapped by 1,4-

cyclohexadiene. In the spin state study described above two radical pairs

were generated (from 4 and 6) at low concentrations of cyclohexadiene and a

single pair (from 4) at high concentrations. However, because 6 is

presumably produced from 4 without a change in spin multiplicity, the spin

state analysis above may still be appropriate; this is strongly supported by

the observation that the ratio C/E was independent of cyclohexadiene

concentration even though the relative amounts of trapping of biradical 4 and

6 varied considerably.

There are several alternatives to the conclusions drawn from the chemical trapping data. First, although the ratio C/E was found to have a value (ca. 0.6) which strongly suggests the presence of singlet 4, the same value could have been obtained if extremely rapid intersystem crossing produced an equilibrium ratio of singlet and triplet 4 at all concentrations of cyclohexadiene. If this were the case, the ratio C/E would reflect a component of both the singlet (C/E > 0.6) and triplet (C/E ca. 0) radical pairs. Another way to explain the results is that k_{isc} and $k_S[SH]$ are competitive, but $k_T[SH]$ is very slow and failed to generate an appreciable amount of the triplet radical pair. It is difficult to imagine a factor that would lead to such an appreciable difference in the reactivity of singlet and triplet 4 toward cylohexadiene. A final possibility, which cannot be ruled out, is that k_{isc} is too slow to produce an observable amount of triplet 4 under the reaction conditions, even if the triplet state is equal to or lower in energy than the singlet. Unfortunately, the lifetime of 1,4-dehydrobenzene biradicals are limited by ring opening and other unimolecular reactions, even in the absence of bimolecular reaction channels. Generation of 1,4-dehydrobenzenes at lower temperature might favor intersystem crossing over other reaction pathways;[22] the rapid aromatization of cyclic diethynyl olefins at ambient temperature, observed by Masamune[23] and Sondheimer[24] and their coworkers, suggests one approach.

Conclusions

The unambiguous CIDNP result obtained in the reaction of 11 compares well with the chemical trapping study which indicates the presence of singlet state intermediates in the reaction of 3. The failure to detect evidence for

the population of triplet **4** or **14** in these studies may be due to the short lifetime of the 1,4-dehydrobenzene intermediates under the reaction conditions. A slow intersystem crossing rate will preclude observation of the triplet biradical even if it is the lowest energy state. The lifetime of 2,3-dialkyl substituted 1,4-dehydrobenzenes may be estimated from the parameters previously obtained for **4**;[2] at 200° C, unimolecular ring opening occurs with a half-life of _ca._ 10^{-8} to 10^{-9} sec. Therefore, if the ground electronic state of 1,4-dehydrobenzenes **4** and **14** is the triplet, population from the singlet must occur with a rate constant $<10^9$ sec.

Experimental Section

General

Descriptions of the NMR, IR and mass spectrometers used and the method of preparation of solution and CIDNP reaction samples have been described elsewhere.[2b]

Preparative VPC was performed on a Varian 90P instrument. Analytical VPC was conducted on either a Perkin-Elmer 3920 or a Perkin-Elmer Sigma 3 chromatograph. Both were equipped with flame ionization detectors (FID) and were interfaced with a Spectra Physics Autolab Stysystem 1 computing integrator. The VPC columns used in the work reported here were the following: for preparative VPC: 10' x 1/4" glass 10% SF-96 on 60/80 Chrom W; for analytical VPC: 9' x 1/8" stainless steel 10% SF-96 on 100/120 Chrom W-AW/DMCS; for VPC-MS analyses: 30 m glass capillary SP2100 wall coated open tubular (WCOT) column.

Synthesis

2-Bromo-3-butyne: A procedure for a similar reaction has been outlined by Ashworth, Whitham and Whiting.[25] A dry ether solution (18 mL) of 1-butyn-3-ol (22.2 g, 0.317 mol) and pyridine (0.22 mL) were placed in a 3-neck flask fitted with an addition funnel, an argon inlet and a reflux condenser. To the argon-flushed flask cooled to 5° C was added an ether solution (12 mL) of freshly distilled PBr_3 (42.5 g, 0.317 mol) over 4 h. Reaction was complete at the end of the addition (VPC analysis on preparative instrument, 45° C). Water was carefully added to the clear orange-brown reaction solution until fuming ceased. The organic phase was separated and washed with 50 mL of an aqueous $NaHCO_3$ solution followed by a wash with 50 mL brine. The ether solution was dried over $MgSO_4$; distillation through a Ta wire column at 1 atm

gave 13.6 g (32% yield) of 2-bromo-3-butyne (>98% pure, as determined by VPC) bp 83-90° C. ^{1}H-NMR (CCl$_4$): δ1.90 (d,3H,J=7), 2.53 (d,1H,J=2.5), 4.51 (d of q,1H,J=7,2.5). IR (thin film): 3300, 2950, 2120, 1430, 1370, 1300, 1180, 1090, 1060, 990, 970, 855 cm^{-1}. Anal. Calcd. for C$_4$H$_5$Br: C, 36.13; H, 3.75. Found: C, 35.95, H, 3.76.

3,4-Dimethyl-hexan-1,5-diyn-3-ol: An oven dried 3-neck flask was fitted with an addition funnel, condenser, thermometer and an argon inlet. Magnesium turnings (2.45 g, 0.10 mol) dry ethyl ether (10 mL) and a small amount of HgCl$_2$ were added. After the solution became cloudy the reaction flask was cooled to 10° C and an ethyl ether (65 mL) solution of 2-bromo-3-butyne (13.6 g, 0.10 mol) was added over 1.5 h. A clear, faint yellow solution resulted. The solution was cooled to -15° C and methyl ethynyl ketone (6.9 g, 0.10 mol) dissolved in ethyl ether (70 mL) was added over 1 h. A white ppt. formed after the addition was one-half complete. After the addition, the solution was warmed to room temperature over 0.5 h and poured into a cold, saturated aqueous NH$_4$Cl solution. The organics were isolated and the aqueous phase was washed three times with ethyl ether. The combined ethyl ether solutions were washed with 150 mL brine and then dried over Na$_2$SO$_4$. Concentration on a rotary evaporator gave a somewhat volatile reddish oil. The crude product was purified by passing through a pad of silica gel with a mixture of pet ether and ethyl ether as eluent (7:3 v/v). Static vacuum distillation (0.03 torr) of the oil gave 8.4 g (>98% pure as determined with preparative VPC) of 3,4-dimethyl-hexan-1,5-diyn-3-ol (70%) as a colorless oil. The alcohol was formed as a mixture of diastereomers (5:1 ratio) which could be separated by preparative VPC (column temperature, 100° C). NMR of major diastereomer (CDCl$_3$): δ1.33 (d,3H,J=7.5), 1.54 (s,3H), 2.19 (d,1H,J=2.5), 2.46 (s,2H,OH,acetylenic H), 2.65 (m,1H,J=7.5,2.5). IR

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(thin film): 3250, 3220, 2980, 2110, 1710, 1440, 1370, 1250, 1090, 1030, 1000, 970, 720 cm^{-1}. Anal. Calcd. for $C_8H_{10}O$: C, 78.65; H, 82.5. Found: C, 78.36; H, 8.23.

2,3-Dimethyl-hexa-1,5-diyn-3-ene (11): A 25 mL 3-neck flask was fitted with an argon inlet, addition funnel and a stopcock through which aliquots could be removed. After flushing with argon, 3,4-dimethyl-hexan-1,5-diyn-ol (1.65 g, 0.011 mol) and pyridine (3.5 mL) were added. The mixture was cooled to 5° C and a solution of POCl$_3$ (1.98 g, 1.2 mL, 0.013 mol) in pyridine (1.7 mL) was added with stirring over 30 min. The reaction was monitored by preparative VPC (column temperature = 98° C). After the addition of POCl$_3$, little reaction had occurred, so the mixture was warmed slowly to r.t. After 1 h at room temperature the reaction was complete. The dark reaction mixture was poured over ice with pet ether and H$_2$O rinses. The organic layer was separated and the aqueous phase was washed 3 times with pet ether. The combined organics were washed with 10% aqueous HCl until acidic by litmus and then washed with H$_2$O to pH 4. The pet ether solution was dried over Na$_2$SO$_4$ and concentrated to give 0.63 g (50% yield) of an orange oil (>95% pure by VPC). Crystallization of cis and trans 2,3-dimethyl-hexa-1,5-diyn-3-ene (ratio 1:3) at -70° C gave further purified product. The geometric isomers were isolated by column chromatography on silica gel (pet ether eluent). Cis isomer: NMR (CDCl$_3$): δ1.88 (s,6H), 3.17 (s,2H). IR (thin film): 3310, 3020, 2935, 2874, 2108, 1445, 1386, 1250, 1156, 1103 cm^{-1}. Trans isomer: NMR (CDCl$_3$): δ2.02 (s,6H), 3.36 (s,2H). IR (thin film): 3318, 2970, 2940, 2872, 2002, 1735, 1445, 1378, 1265, 1235, 1166, 1098, 800 cm^{-1}. HRMS: precise mass calcd. for C_8H_8, 104.0625; found for cis 11, 104.0623; found for trans 11, 104.0622.

Thermal Reactions

Reaction of 2,3-dimethyl-hexa-1,5-diyn-3-ene (11) in chlorinated solvents: CCl_4 (MCB spectral quality) was used without additional purification. Hexachloroacetone was purified by repeated distillation at 50 torr through a vacuum-jacketed glass helices-packed column. 11 was purified by preparative VPC (column temperature, 85° C). n-Octane was used as an internal standard in the thermal reactions. Yields of products were determined by reference to the internal standard with the assumption that the response factor of the starting material and products were the same.[26] Pyrolyzed solutions were dark, guinness-brown, suggesting the occurrence of substantial polymerization. Reaction product 12 was isolated from the CCl_4 reaction mixture by preparative VPC (column temperature, 135° C) and identified by NMR, IR and HRMS (see below). Compound 13 was identified by its mass spectrum (m/e 140). No evidence for high molecular weight products, formed by combination of the radical pairs generated by transfer of chlorine (eg. Scheme IV), was detected by VPC-MS analysis of the hexachloroacetone solution reaction. In the CCl_4 reaction a product with m/e 256, 258, 260, 262 was detected; this may have been formed by cage combination of the aryl radical 15 with the trichloromethyl radical (Scheme IV). 1,4-dichloro-2,3-dimethyl-benzene (12): NMR (CCl_4): δ 2.33 (s,6H), 6.98 (s,2H). IR (CCl_4): 3020, 2940, 1875, 1458, 1413, 1389, 1264, 1161, 1136, 1030, 833, 590 cm^{-1}. HMRS: precise mass calcd. for $C_8H_8Cl_2$, 173.0003; found, 174.9999.

Reaction of 4,5-diethynyl-oct-4-ene (3) in cyclohexadiene-d_0 and -d_4: Compound 3 was isolated >99% pure by preparative VPC and promptly dissolved in chlorobenzene to give a solution 0.01 M in 3. n-Undecane was added as an internal standard and the initial concentration of 3 was determined by comparison of the integrated analytical VPC peak areas. Cyclohexadiene-d_0

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and $-d_4$ were added to the chlorobenzene solution of 3 in a pyrolysis tube which was promptly sealed. After reaction for 15 min at 195° C, the solutions were very light yellow colored. The reacted solutions were analyzed by analytical VPC (initial temp. 150° C for 15 min; increase at 5° C/min; hold at 220° C for 20 min) and the product yields determined by reference to the internal standard. The relative yields of $10-d_0$, $-d_1$ and $-d_2$ were determined by VPC-MS analysis (WCOT capillary column; initial temp. 110° C; increase at 4° C/min; hold at 220° C). The ratio of cyclohexadiene-d_0 and $-d_4$ used was 1:4. With this ratio, $10-d_0$ and $-d_2$ were formed in nearly equal yield (k_H/k_D is 4). The ratio of C/E was determined as follows: cage escape (E) is the only source of $10-d_1$; escape gives $10-d_0$, $-d_1$ and $-d_2$ in the ratio 1:2:1. Therefore, the escape component of $10-d_0$ and $-d_2$ is 1/2 the yield of $10-d_1$. The remainder of $10-d_0$ and $-d_2$ was formed by cage reaction (C) and was added to the yield of $C_{18}H_{22}$ and $C_{18}H_{24}$ species to give the yield of cage products.
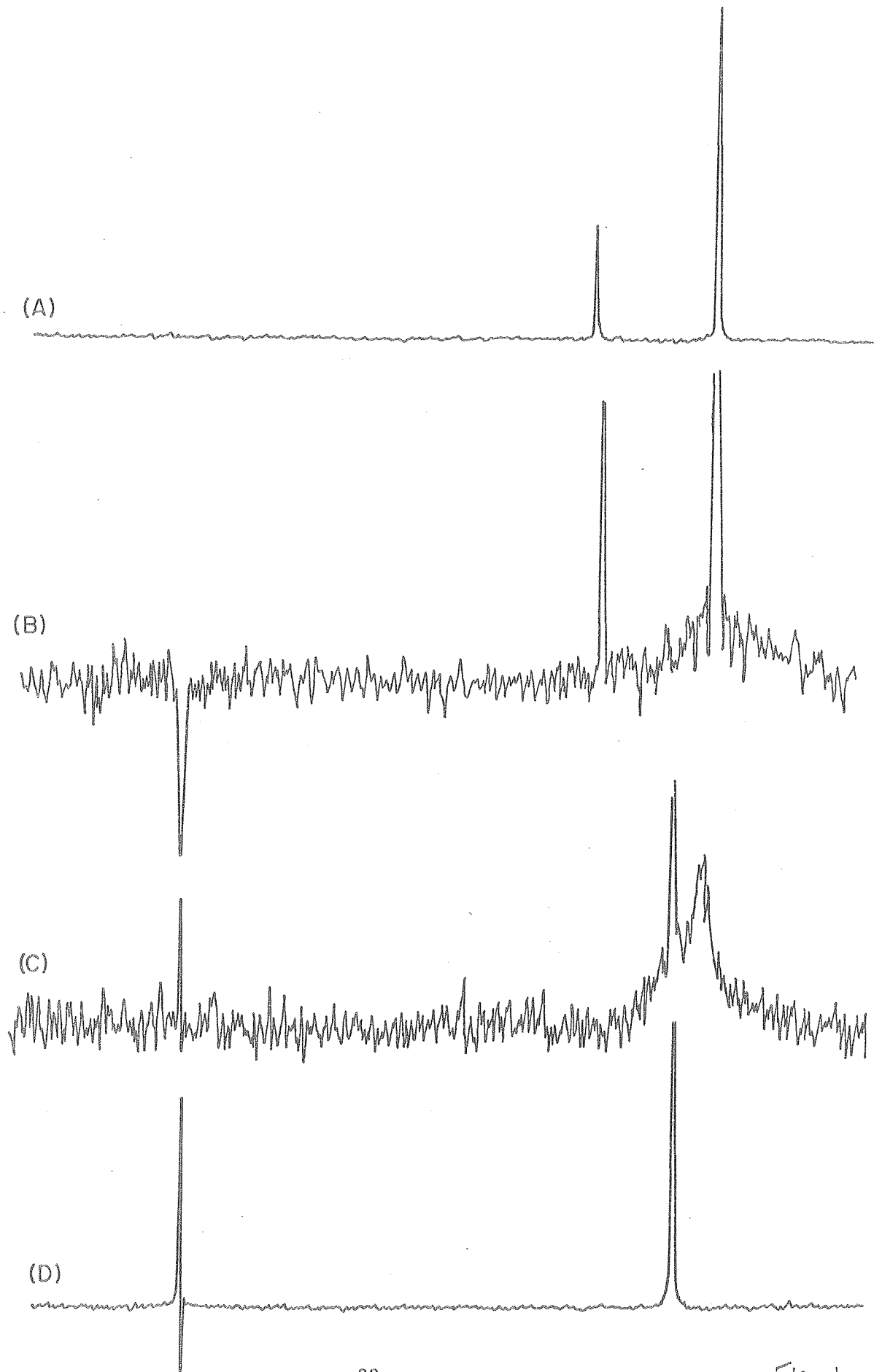
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15. For a recent study see Engel, P.S.; Bishop, D.J.; Page, M.A.; J. Am. Chem. Soc., 1978, 100, 7009. Perhaps the most convincing demonstration of a SCE is that of Closs, G.L.; Trifnac, A.D.; J. Am. Chem. Soc., 1969, 91, 4554. For a less supportive discussion see Koenig, T., in "Free Radicals", Vol. I, Kochi, J.K., Ed., J. Wiley and Sons, New York,
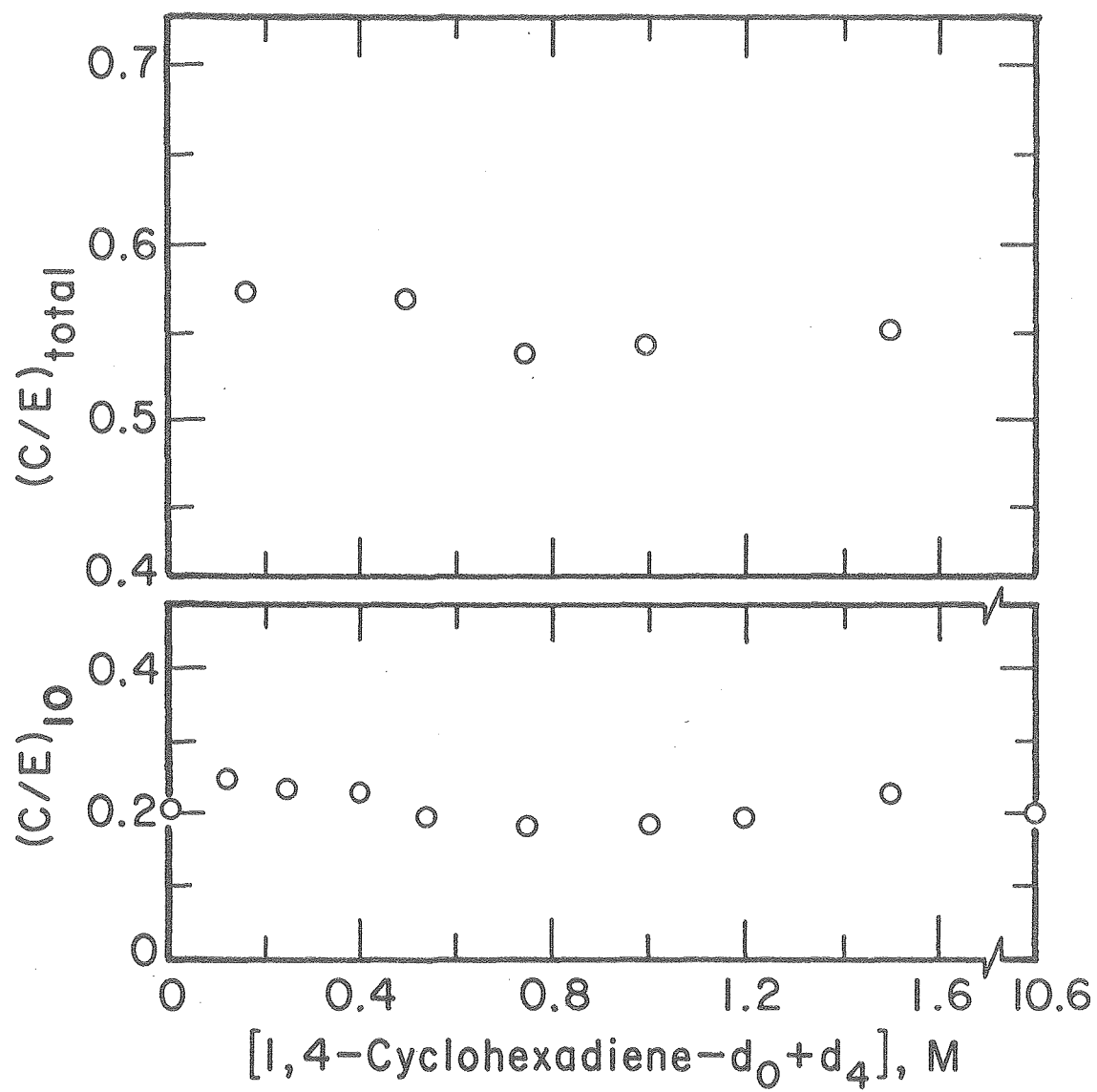
1973, Chapter 3.

16. The term "cage reaction" as applied in this discussion is meant to denote bimolecular reactions which take place within the geminate radical pair, ie., combination and disproportionation.

17. Since the lifetime of solvent-caged radical pairs is ca. 10^{-10} and the rate of intersystem crossing is ca. 10^8 sec^{-1},[12] triplet-singlet interconversion should have an insignificant effect on the product distibution.

18. That $C_{18}H_{22}$ and $C_{18}H_{29}$ hydrocarbons are formed solely by cage combination is demonstrated by the observation that, when 3 was allowed to react in the presence of cyclohexadiene-d_o and -d_4, these products contained only 0, 1 and 2 deuteria/molecule. Random combination of aryl and cylohexadienyl radicals would have led to appreciable formation of the d_1 and d_3 isomers.

19. The ratio of cyclohexadiene-d_o and -d_4 was held constant but the total concentration of trapping agent was varied.

20. At low concentrations of trapping agent, the yield of 10 and C_{18} products was very small. Because 10 overlaps slightly with unimolecular product 9 in the VPC trace, small amounts of 10 were difficult to accurately measure. Likewise, because they refer to several isomeric, long retention time products, VPC integration of C_{18} products was not accurate when low yields were produced in the reaction.

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Figure 1.   CIDNP observed during reaction of a hexachloroacetone solution of $\underset{\sim}{11}$.   (A) NMR of solution before reaction.   (B) Signals observed during reaction at 160°C.   (C) Room temperature spectrum after complete reaction of $\underset{\sim}{11}$.   (D) Spectrum of $\underset{\sim}{12}$ in CCl_4.

Figure 2.   Ratio of cage to escape products (C/E) observed in the reaction of $\underset{\sim}{3}$ (0.01 M, 195°C) as a function of 1,4-cyclohexadiene concentration.   Upper plot shows C/E for both $\underset{\sim}{10}$ and C_{18} combination products.   Lower plot shows C/E for product $\underset{\sim}{10}$ alone.

Figure 3.   Ratio of cage to escape products (C/E) observed in the reaction of $\underset{\sim}{3}$ (0.01 M, 195°C) in bromobenzene solution as a function of added 1,4-cyclohexadiene.   Upper plot shows C/E for $\underset{\sim}{10}$ and C_{18} combination products.   Lower plot shows C/E for product $\underset{\sim}{10}$ alone.
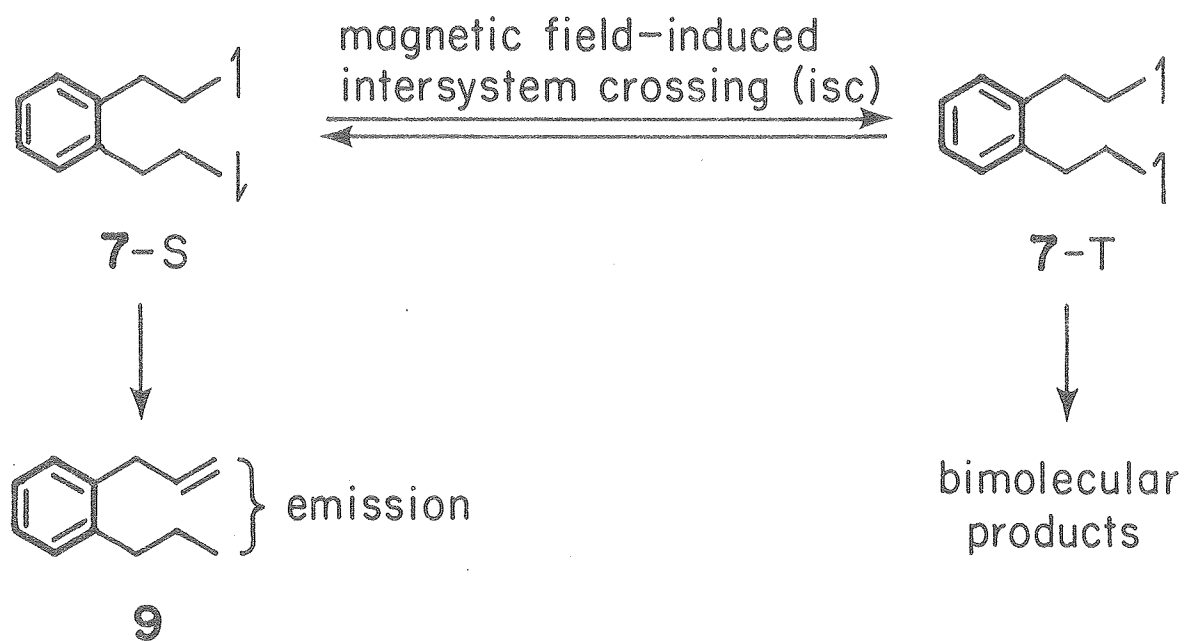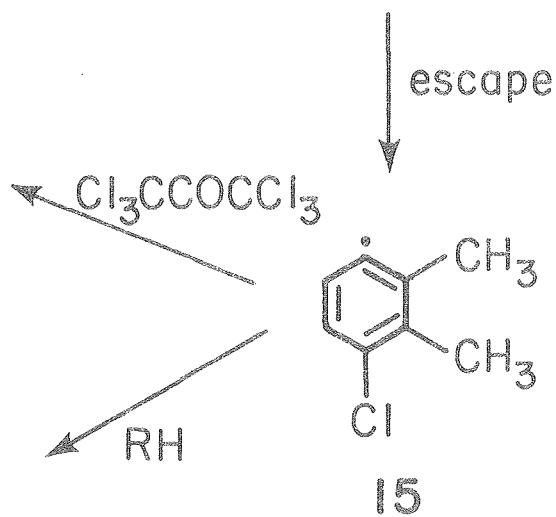
Fig. 1

Fig. 2

Fig. 3

Scheme I

Scheme II

magnetic field-induced intersystem crossing (isc)

7-S

7-T

9 } emission

bimolecular products

Scheme III

Scheme IV

Scheme IV

4

d_0/d_4

cage reaction

escape

10 $(d_0 + d_2)$
+
$C_{18}H_{22}$ and $C_{18}H_{24}$ combination products

10 $(d_0 + d_1 + d_2)$
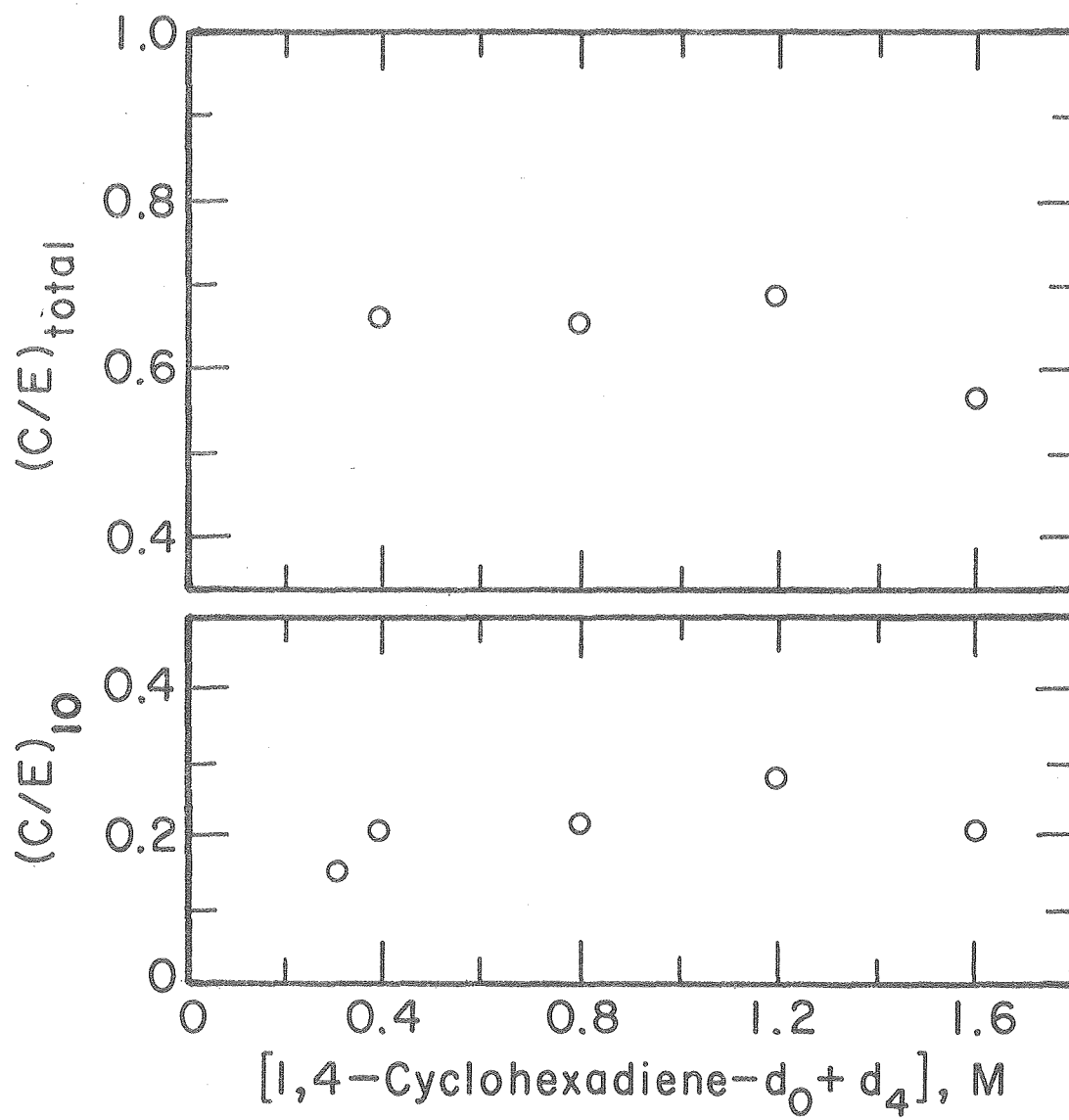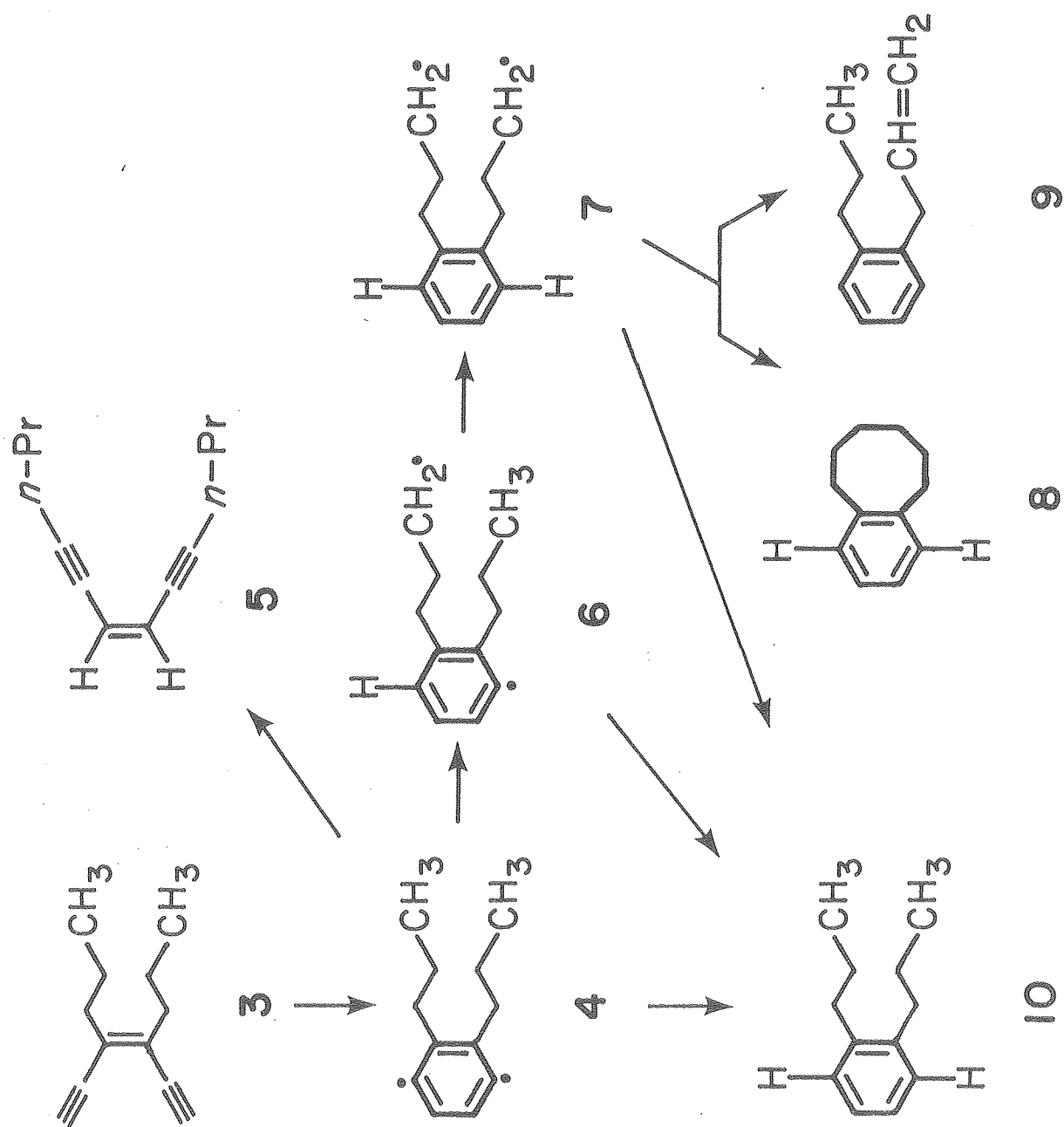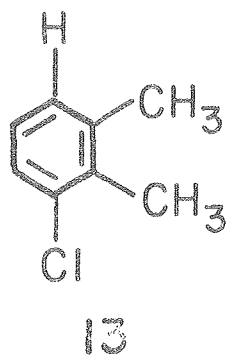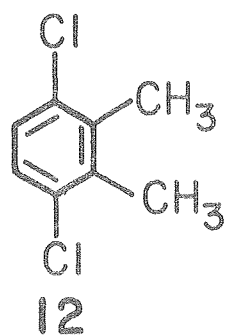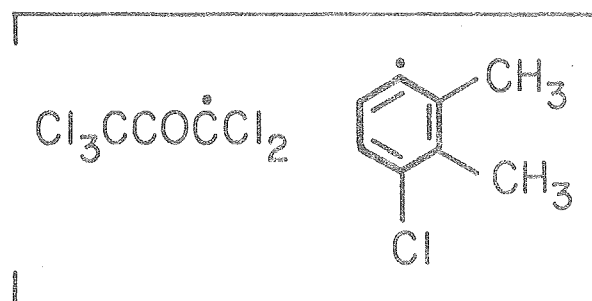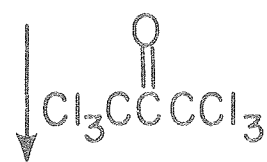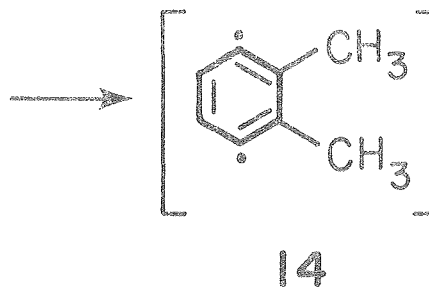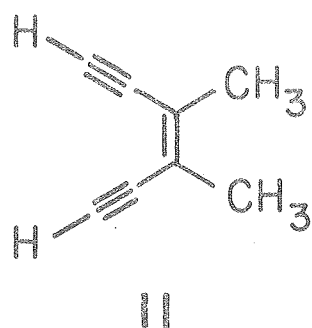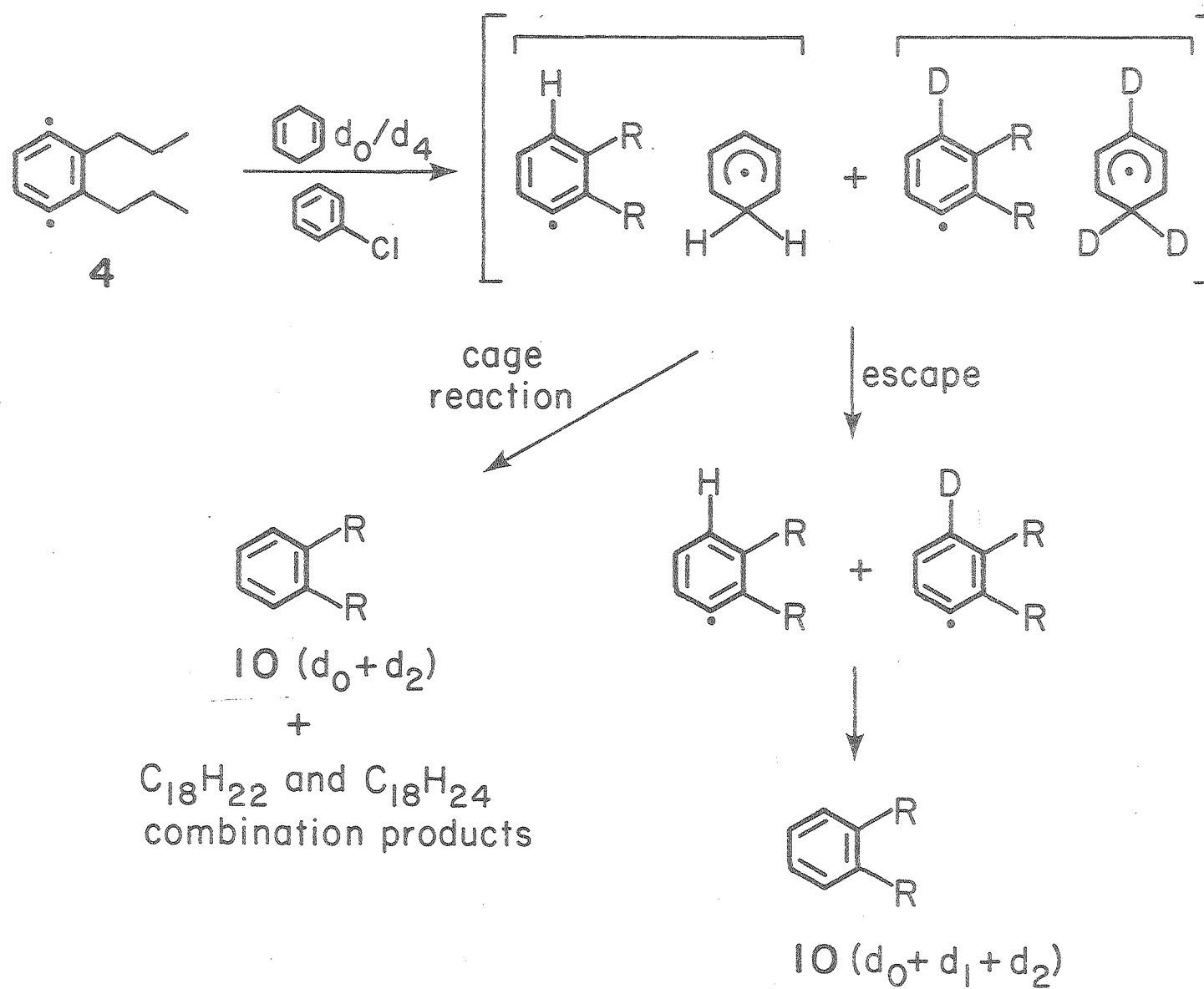
Table 1. Calculated Energies of 1,4-Dehydrobenzene Structures

	Relative Energy of Structures (kcal/mol)		
	$\underset{\sim}{1}$ (Triplet)	$\underset{\sim}{1}$ (Singlet)	$\underset{\sim}{2}$ (Singlet)
Wilhite, Whitten (1971)[4] SCF-MO-CI	0	+3.45	--
Dewar et al. (1974)[5] MINDO|3; lim. CI	+5	$0(\Delta H_f = +117)$	+36
Washburn et al. (1979)[8] Ab initio, 4-31G (no CI)	0	(+82)	+94
Mueller (1973)[7] Modified MINDO|2 (no CI)	0	(+24)	+18
Noell and Newton (1979)[6] Ab initio GVB; 4-31G	+1.4	0	--

Table 2. Products Formed on Reaction of $\underset{\sim\sim}{11}$ (10^{-2} M) in Solution at 190°C

	Absolute Yield (%)	
Solvent	$\underset{\sim\sim}{12}$	$\underset{\sim\sim}{13}$
Hexachloroacetone	17	5
CCl_4	20	5